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(54) AIR BAG GAS GENERATING AGENT

(57) An object of this invention is to provide an air bag azide-free gas generating composition which can pronouncedly reduce the concentrations of toxic components in the after gas, especially both concentrations of CO and NO_x while retaining the desired advantages of azide-free gas generating compositions. The air bag gas generating composition of the invention is an azide-free gas generating composition comprising a nitrogen-containing organic compound and an oxidizing agent as active components, and further contains, as a burning catalyst, at least one metallic oxide selected from the group consisting of molybdenum oxides, tungsten oxides and metallic oxides having a BET specific surface area of at least 5 m^2/g.

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Description

Technical Field

The present invention relates to an air bag gas generating composition and an air bag inflator.

The air bag gas generating composition of the present invention has the preferred advantages that toxic components such as CO are present at very low concentrations in a gas evolved on combustion of the composition (hereinafter referred to as "after gas"), and that the composition is far safer than conventional azide-based gas generating compositions.

The air bag inflator of this invention can further reduce the CO concentration in the after gas.

Background Art

A demand for air bag systems is phenomenally increasing in view of the current more and more rigorous requirements concerning the safety of automobiles. The air bag system is adapted to inflate a nylon bag (air bag) stowed in the steering wheel assembly, the dashboard of a car or the like on sensing a car crash occurring at high speed, thereby protecting the driver and other passengers from being injured or killed by the impact against the internal equipment of the car. The bag is inflated with a gas evolved on combustion or decomposition of the gas generating composition held in the air bag system.

Preferably air bag gas generating compositions meet mainly four requirements. The first requirement is that the gas generating compositions have adequate burning velocity. If the burning velocity is low, the air bag can not instantly inflate, failing to protect the passengers. The second requirement is that the gas generating compositions have a low impact ignitability (ignition sensitivity to impact). High impact ignitability tends to trigger explosion or detonation in the manufacturing process as in mixing or molding, involving high risks in handling. The third requirement is that the gas temperature is low. The air bag deflates by release of the gas after inflation for passengers' escape to outdoor. Yet, passengers may suffer a burn if exposed to a high temperature gas. The air bag may fracture on contact with a high temperature gas, thereby becoming unfit in function or may become ignited, thereby inducing a fire. The fourth requirement is that the concentrations of toxic components such as CO and NO_x in the gas are low. If the gas contains toxic components at high concentrations, passengers may suffer gas poisoning in release of the gas. Generally the concentrations of CO and NO_x in a gas evolved on combustion of an organic compound are mutually inverse (in inverse proportion). The two components are so correlated that a decrease in the concentration of one component leads to an increase in the concentration of the other. Thus it is considered very difficult to decrease the concentrations of both components at the same time.

Sodium azide-based gas generating compositions which are in common use today show adequate burning velocity and gas temperature and generate nontoxic nitrogen gas for the most part but are defective in having high impact ignitability. Further, the decomposition of sodium azide used as a gas generating base may bring about a fire or may produce a toxic fume. Sodium azide reacts with an oxidizing agent to liberate toxic substances such as sodium oxide, sodium hydroxide, etc., calling for careful handling and essentially necessitating equipment for ensuring safety. Furthermore, sodium azide becomes less combustible on absorption of moisture, making it necessary to take measures against the absorption of moisture. In addition, sodium azide which is highly toxic would be likely to cause serious environmental pollution by the spread which may occur if an air bag-equipped car has fallen into a river or the sea.

On the other hand, Japanese Unexamined Patent Publications Nos.32689/1994, 32690/1994 and 227884/1994 disclose azide-free gas generating compositions proposed by the present inventors, the compositions comprising a nitrogen-containing organic compound and an oxidizing agent as active components. The disclosed gas generating compositions are comparable to conventional azide-based gas generating compositions in adequate amount of generated gas, burning velocity and gas temperature. Further, the disclosed compositions are relatively low in impact ignitability and significantly low in explosion risks and toxicity, namely have the advantages which are not found in azide-based gas generating compositions. Moreover, the compositions are inexpensive. While toxic components such as CO and NO_x exist at low concentrations in a gas evolved by combustion of said azide-free composition, assuring the practical use of the composition, a further reduction in the concentrations of toxic components is desired.

Japanese Unexamined Patent Publication No. 238867/1993 proposes the use of metallic oxides having a specific surface area of at least 5 m^2/g (especially oxides of metals of atomic numbers 21 (Sc) to 30 (Zn)) in a gas generating composition. However, the subject matter disclosed in the publication is a gas generating composition comprising sodium azide as a gas generating base. The metallic oxide is merely added to enhance mainly the burning velocity and the ignitability. Further, a metallic oxide with its effect specifically described in the publication is only Fe_2O_3.

Disclosure of the Invention

The inventors of the present invention conducted extensive research to overcome the foregoing problems and

found that when a specific metallic oxide and/or a metallic oxide having specific properties is incorporated as a burning catalyst into an azide-free gas generating composition, the concentrations of toxic components in the after gas, especially both CO and NO_x, can be markedly reduced while retaining the preferred advantages of the azide-free gas generating composition. Another finding was that the concentrations of toxic components would be further reduced if an oxidizing agent is placed on at least one part of a passage for the release of the gas within an air bag inflator. The present invention was completed based on these novel findings.

According to the invention, there is provided an air bag azide-free gas generating composition comprising a nitrogen-containing organic compound and an oxidizing agent as active components, and further containing, as a burning catalyst, at least one metallic oxide selected from the group consisting of molybdenum oxides, tungsten oxides and metallic oxides having a BET specific surface area of at least 5 m^2/g.

According to the invention, there is also provided an air bag inflator wherein an air bag gas generating composition is held in a combustion chamber and wherein an oxidizing agent for external use is disposed on at least one part of a passage for releasing into an air bag a gas evolved on combustion of the air bag gas generating composition.

The active components of the air bag gas generating composition according to the invention are a nitrogen-containing organic compound serving as a gas generating base, an oxidizing agent and a specific burning catalyst.

Organic compounds having at least one nitrogen atom per molecule can be used as the nitrogen-containing organic compound. Specific examples of the nitrogen-containing organic compound to be used are amino group-containing organic compounds, nitramine group-containing organic compounds, nitrosoamine group-containing organic compounds, etc.

Specific examples of amino group-containing organic compounds that can be used are azodicarbonamide, azodicarboxylic acid and a salt thereof (alkali metal salt, alkaline earth metal salt, etc.), urea, hexamethylenetetramine, aminoguanidine bicarbonate, triaminoguanidine, biuret, cyanoguanidine, nitroguanidine, dicyandiamide, hydrazide, etc. Useful hydrazides include conventional hydrazides such as acetohydrazide, 1,2-diacetylhydrazide, laurohydrazide, salicylohydrazide, oxalohydrazide, oxalodihydrazide, carbohydrazide, adipohydrazide, sebacohydrazide, dodecanediohydrazide, isophthalohydrazide, methyl carbazate, semicarbazide, formhydrazide, 1,2-diformylhydrazine and so on.

Examples of nitramine group-containing organic compounds that can be used include aliphatic and alicyclic compounds containing one or more nitramine groups as substituents such as dinitropentamethylenetetramine, trimethylenetrinitroamine (RDX), tetramethylenetetranitroamine (HMX) etc.,

Examples of nitrosoamine group-containing organic compounds that can be used include aliphatic and alicyclic compounds containing one or more nitrosoamine groups as substituents such as dinitrosopentamethylenetetramine (DPT), etc.

Among them, amino group-containing organic compounds are preferred and azodicarbonamide is more preferred. Such nitrogen-containing organic compounds can be used either alone or in combination. Commercially available nitrogen-containing organic compounds can be used as such. The particle size of the nitrogen-containing organic compound is not specifically limited and can be suitably selected from a wide range depending on the amount of the compound, proportions with other components, volume of the air bag and other factors.

Useful oxidizing agents are not specifically limited and can be suitably selected from those conventionally used in the art. Preferred oxidizing agents are those which can generate and/or supply oxygen at high temperatures. Examples are oxyhalogen acid salts, nitrates, nitrites, metallic peroxides, hyperoxides, ozone compounds, etc.

Oxyhalogen acid salts which can be used herein include conventional ones such as perhalogenates, halogenates, etc. Examples of useful perhalogenates are alkali metal salts such as lithium perchlorate, potassium perchlorate, sodium perchlorate, lithium perbromate, potassium perbromate, sodium perbromate and like alkali metal salts, magnesium perchlorate, barium perchlorate, calcium perchlorate, magnesium perbromate, barium perbromate, calcium perbromate and like alkaline earth metal salts, ammonium perchlorate, ammonium perbromate and like ammonium salts, etc. Examples of useful halogenates are alkali metal salts such as lithium chlorate, potassium chlorate, sodium chlorate, lithium bromate, potassium bromate, sodium bromate and like alkali metal salts, magnesium chlorate, barium chlorate, calcium chlorate, magnesium bromate, barium bromate, calcium bromate and like alkaline earth metal salts, ammonium chlorate, ammonium bromate, and like ammonium salts, etc. Among them, alkali metal salts of halogen acids and oxyhalogen acids are preferred.

Examples of useful nitrates are lithium nitrate, sodium nitrate, potassium nitrate and like alkali metal salts, magnesium nitrate, barium nitrate, strontium nitrate and like alkaline earth metal salts, ammonium nitrates and like ammonium salts among which alkali metal salts are preferred.

Examples of useful nitrites are lithium nitrite, sodium nitrite, potassium nitrite and like alkali metal salts, magnesium nitrite, barium nitrite, calcium nitrite and like alkaline earth metal salts, etc.

Examples of metallic peroxides for use herein are lithium peroxide, sodium peroxide, potassium peroxide and like alkali metal salts, magnesium peroxide, calcium peroxide, barium peroxide and like alkaline earth metal salts, etc.

Examples of hyperoxides for use herein are sodium hyperoxide, potassium hyperoxide and like alkali metal compounds, calcium hyperoxide, strontium hyperoxide, barium hyperoxide and like alkaline earth metal compounds, rubidium hyperoxide, cesium hyperoxide, etc.

Examples of ozone compounds to be used are compounds represented by the formula MO_3 wherein M is an element of Group Ia in the periodic table such as Na, K, Rb, Cs and the like.

Optionally molybdenum disulfide and like metal sulfides, bismuth-containing compounds, lead-containing compounds, etc. are usable as oxidizing agents.

Among these oxidizing agents, oxyhalogen acid salts, nitrates, nitrites, etc. are desirable and oxyhalogen acid salts and nitrates are more desirable.

These oxidizing agents can be used either alone or in combination. The shape, particle size and other conditions of the oxidizing agent are not critical and can be selected according to, for example, the amount of the oxidizing agent, proportions with other components, and volume of air bag.

The amount of the oxidizing agent to be used is a stoichiometric amount sufficient to completely oxidize and burn the nitrogen-containing organic compound, calculated on the basis of the amount of oxygen. The amount of the oxidizing agent can be properly selected from a wide range since the burning velocity, burning temperature (gas temperature), composition of combustible gas, etc. can be adjusted as desired by suitably changing the proportions of the nitrogen-containing organic compound and the oxidizing agent used. For example, the amount of the oxidizing agent is about 10 to about 400 parts by weight, preferably about 100 to about 240 parts by weight, per 100 parts by weight of the nitrogen-containing organic compound.

Essentially the gas generating composition of the invention contains, in addition to the above two components, at least one metallic oxide selected from the group consisting of molybdenum oxides, tungsten oxides and metallic oxides having a BET specific surface area of at least 5 m^2/g. The incorporation of the metallic oxide can pronouncedly reduce the concentrations of toxic components such as CO and NO_x in the after gas. While the reason why such remarkable effect can be achieved remains to be clarified, the inventors' research has found that presumably the azide-free gas generating composition comprising, for example, azodicarbonamide as a gas generating base and oxyhalogen acid salt as an oxidizing agent undergoes a smooth reaction between the two components in nearly stoichiometric amounts since the thermal decomposition temperature of oxyhalogen acid salt is lowered closely to the thermal decomposition temperature of azodicarbonamide by the addition of the metallic oxide to the combustible reaction system although a great difference lies in the thermal decomposition temperature between the two components.

Examples of molybdenum oxides which can be used include conventional ones such as molybdenum oxide (VI), other oxygen-containing molybdenum compounds which can yield molybdenum oxide (VI) when heated, molybdic acid, metal salts of molybdic acid, etc. Useful oxygen-containing molybdenum compounds include, for example, molybdenum hydroxides and molybdenum oxides such as MO_2O_5, MO_3O_8, MO_3O_{23}, MO_9O_{29}, etc. Examples of useful metal salts of molybdic acid are cobalt molybdate, nickel molybdate and like salts of Group VIII metals, etc. Among them, molybdenum oxide (VI) and metal salts of molybdic acid are preferred, and molybdenum oxide (VI) is more preferred.

Examples of useful tungsten oxides include conventional ones such as tungsten oxide (VI), other oxygen-containing tungsten compounds which can yield tungsten oxide (VI) by heating, tungstic acid, metal salts of tungstic acid, etc. Useful oxygen-containing tungsten compounds include, for example, tungsten oxides such as WO_2, WO_3, $WO_3 \cdot H_2O$, etc. Examples of useful metal salts of tungstic acid are potassium tungstate, calcium tungstate, sodium tungstate, magnesium tungstate, cobalt tungstate, nickel tungstate, iron tungstate, etc. Among them, tungsten oxide (VI) and metal salts of tungstic acid are preferred, and tungsten oxide (VI) and iron tungstate are more preferred.

Metallic oxides having a BET specific surface area of at least 5 m^2/g are not specifically limited insofar as they have the above-defined specific surface area and they are metallic oxides other than said molybdenum oxides and tungsten oxides. Examples of metallic oxides to be used include the oxides of elements of 3rd and 4th periods in the periodic table such as copper oxide, nickel oxide, cobalt oxide, iron oxide, chromium oxide, magnesium oxide, aluminum oxide, zinc oxide, manganese oxide, etc. Among them, preferred are the oxides of elements of Groups VIII and Ib such as copper oxide, nickel oxide, cobalt oxide, etc. and more preferred is copper oxide. Metallic oxides having a BET specific surface area of at least 5 m^2/g can be used either alone or in combination. Useful metallic oxides are those having a BET specific surface area of at least 5 m^2/g, preferably at least 10 m^2/g, more preferably at least 40 m^2/g.

Metallic oxides having a large specific surface area can be prepared by conventional methods. For example, copper oxide can be prepared using copper nitrate as the starting material, as by a process comprising adding warm water of at least 60°C to basic copper nitrate to yield basic copper nitrate particles, grinding the particles and calcining the fine particles at about 300 to about 500°C (Japanese Unexamined Patent Publication No.301513/1989), a process comprising adding alkali to an aqueous solution of copper nitrate, for neutralization to give copper nitrate particles, filtering and drying the particles and calcining the particles at about 200 to about 500°C (Japanese Unexamined Patent Publication No.145422/1990), and so on. Copper nitrate can be prepared also by subjecting metallic hydroxide or carbonate to low temperature plasma treatment (Japanese Unexamined Patent Publication No.26810/1990).

Among the three types of burning catalysts, molybdenum oxides and tungsten oxides have the preferred properties of coexisting with a nitrogen-containing organic compound such as azodicarbonamide for a long term while inducing substantially no decomposition of the nitrogen-containing organic compound. Generally the concentrations of CO and NO_x in a gas evolved on combustion of the nitrogen-containing organic compound are inversely proportional to each other. That is, the concentrations of the two toxic components are so correlated that a reduction in the concentration of

one component leads to an increase in the concentration of the other. Therefore it is considered very difficult to decrease the concentrations of both components at the same time. Molybdenum oxides and tungsten oxides also have the favorable property of appreciably decreasing the concentrations of both components in the after gas at the same time.

There is no specific restriction on the particle size of molybdenum oxides, tungsten oxides and metallic oxides having a BET specific surface area of at least 5 m^2/g. The particle size of these oxides can be suitably selected from a wide range depending on their amounts, proportions with other components, structure of air bag, shape, volume and other factors. The amount of these metallic oxides is not critical and can be properly selected from a wide range according to said conditions. Generally the amount is about 0.1 to about 50 parts by weight per 100 parts by weight of the nitrogen-containing organic compound. The desired amount from the viewpoints of stabilizing the amount of generated gas and the combustibility is about 0.5 to about 30 parts by weight per 100 parts by weight of the nitrogen-containing organic compound. When using an oxygen-containing molybdenum compound yielding molybdenum oxide (VI) by heating or oxygen-containing tungsten compound yielding tungsten oxide (VI) by heating, the amount of the compound is so adjusted that the produced molybdenum oxide (VI) or the produced tungsten oxide (VI) is present in the above-specified amount range.

The air bag gas generating composition of the invention may contain, in addition to said three essential components, a burn modifier, an antidetonation agent, a burning velocity control catalyst and the like within the range which does not impair the properties of the composition.

The burn modifier is generally used to lower the burning temperature or the gas temperature. Specific examples of such modifier are hydroxides of aluminum and the like, carbonates, bicarbonates and oxides of alkali metals such as sodium, potassium and the like, carbonates and bicarbonates of alkaline earth metals such as calcium, magnesium, barium, strontium, etc. Among them, hydroxides, carbonates and the like are preferred, and hydroxides are more preferred. The amount of the burn modifier to be used is not critical and can be selected from a wide range. The amount of the modifier is less than 50 parts by weight, preferably less than 20 parts by weight, per 100 parts by weight of the total amount of the nitrogen-containing organic compound and the oxidizing agent.

The antidetonation agent is used to avoid the detonation which would occur if the gas generating composition is wrapped in flames or subjected to great impact in the course of manufacture, transportation, storage or the like. The addition of such antidetonation agent can further enhance the safety of the gas-generating composition in various stages of manufacture, transportation, storage or the like. As the antidetonation agent, known substances can be used. Thus, for example, metallic oxides such as bentonite, alumina, diatomaceous earth, silicon dioxide, etc. and carbonates and bicarbonates of metals such as Na, K, Ca, Mg, Zn, Cu, Al, etc. can be mentioned. Carbonates and bicarbonates of alkali metals or alkaline earth metals function also as the burn modifier as described above. The amount of such antidetonation agent to be used is not critical and can be suitably selected from a broad range. Generally, the amount of the agent is about 5 to about 30 parts by weight per 100 parts by weight of the total amount of the nitrogen-containing organic compound and the oxidizing agent.

The burning velocity control catalyst is used chiefly to control the burning velocity. Such burning velocity control catalysts include, for example, (a) the oxides, chlorides, carbonates and sulfates of elements of 4th to 6th periods in the periodic table (except for molybdenum oxides, tungsten oxides and carbonates of alkali metals or alkaline earth metals) such as zinc carbonate, iron chloride, lead oxide, titanium oxide, banadium oxide, cerium oxide, holmium oxide, calcium oxide, ytterbium oxide, etc., and (b) cellulose compounds such as carboxymethyl cellulose, hydroxymethyl cellulose, their ethers, microcrystalline cellulose particles, etc. and (c) organic high molecular weight compounds such as soluble starch, polyvinyl alcohol, partially saponified products thereof, etc. The particle size of the burning velocity control catalyst is not critical and can be suitably selected. These burning velocity control catalysts can be used either alone or in combination. The amount of the burning velocity control catalyst to be used is not critical and can be suitably selected from a broad range. Generally, however, the amount of the catalyst is about 0.1 to about 50 parts by weight, preferably about 0.2 to about 10 parts by weight, per 100 parts by weight of the total amount of the nitrogen-containing organic compound and the oxidizing agent.

The air bag gas generating composition of the invention may contain additives conventionally used for this purpose within the range which does not impair the desirable properties of the composition.

The air bag gas generating composition of the invention contains, among the above-mentioned components, a compound which induces the decomposition of the nitrogen-containing organic compound, such as azodicarbonamide and the like. Stated more specifically, such compound includes, for example, compounds containing an alkali component or those capable of liberating an alkali component on decomposition, namely compounds serving as a kind of oxidizing agent such as calcium peroxide and the like, and compounds serving as a burning catalyst such as copper oxide, chromium oxide, manganese oxide and the like. Consequently when these decomposition-inducing compounds are used as the component of the air bag gas generating composition of the invention, it is desirable to treat the surface of the gas generating base and/or the decomposition-inducing compound. Preferably a coupling agent, chelating agent or the like is used in the surface treatment.

Useful coupling agents include conventional coupling agents such as silane-based, titanate-based and aluminum-

based coupling agents, etc.

Specific examples of silane-based coupling agents which can be used herein are γ-aminopropyltriethoxysilane, N-β-(aminoethyl)-γ-aminopropyltriethoxysilane, N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane, N-β-(aminoethyl)-γ-aminopropylmethyldimethoxysilane,N-phenyl-γ-aminopropyltrimethoxysilane, γ-ureidopropyltriethoxysilane and like aminosilane-based coupling agents, γ-glycidoxypropyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ-glycidyloxypropyltrimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane and like epoxysilane-based coupling agents, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(β-methoxyethoxy)silane and like vinylsilane-based coupling agents, γ-mercaptopropyltrimethoxysilane and like mercaptosilane-based coupling agents, γ-methacryloyloxypropyltrimethoxysilane and like acrylsilane-based coupling agents, methyltrimethoxysilane, methyltriethoxysilane, γ-chloropropyltrimethoxysilane, trifluoromethyltrimethoxysilane and like silane-based coupling agents represented by the formula $RSi(OR')_3$ wherein R is a straight-chain or branched-chain alkyl group of about 1 to about 4 carbon atoms which may be substituted by at least one halogen atom, and R' is a straight-chain or branched-chain alkyl group of about 1 to about 4 carbon atoms.

Examples of useful titanate-based coupling agents are isopropyltriisostearoyl titanate, isopropyltrisisodecylbenzenesulfonyl titanate, isopropyltris-n-decylbenzenesulfonyl titanate, isopropyltris(dioctylpyrophosphate)titanate, tetraisopropyl-bis(dioctylphosphite)titanate, tetraoctyl-bis(ditridecylphosphite)-titanate, tetra(2,2-diallyloxymethyl-1-butyl)-bis(ditridecylphos-phite)titanate, bis(dioctylpyrophosphate)oxyacetate titanate, bis(dioctylpyrophosphate)ethylene titanate, isopropyltrioctanoyl titanate, isopropyldimethacrylisostearoyl titanate, isopropylisostearoyldiacryl titanate, isopropyltri(dioctylphosphate)titanater isopropyltricumylphenyl titanate, ispropyltri(N-aminoethyl • aminoethyl)titanate, dicumylphenyloxyacetate titanate, diisostearoylethylene titanate, etc.

Examples of useful aluminum-based coupling agents are aluminum monoacetyl acetonate-bis(ethylacetoacetate), aluminum tris(acetylacetate), acetoalkoxyaluminum diisopropylate, etc.

These coupling agents can be used either alone or in combination.

The surface treatment using a coupling agent can be done by conventional methods such as a wet method or a drying method.

The wet method comprises mixing the component to be treated and a solution or a dispersion of the coupling agent, separating the treated component from the mixture and drying the component. The coupling agent is soluble or dispersible in water, an aqueous solution of acetic acid, methanol, ethanol, cellosolve, alkylamine, alkylolamine or like organic solvents or a mixture of these solvents. The concentration of the coupling agent is not specifically limited and can be suitably selected from a wide range. But it is usually about 0.1 to about 5% by weight, preferably about 0.5 to about 2% by weight. The treated component is separated by conventional methods such as filtration, centrifugation, decantation, etc. When the dried component is an agglomerate, it may be ground by a conventional method. Optionally a solution or a dispersion of the component to be treated is mixed with a solution or a dispersion of the coupling agent, the treated component is separated from the mixture, and the component is dried. Useful solvents for dissolving or dispersing the component to be treated include the solvents exemplified above. The wet method can also be performed at an elevated temperature or by heating when so required. In this case, the desired temperature is about 30 to about 100°C.

The drying method comprises adding a coupling agent or a solution or a dispersion of the coupling agent to a powder of the component to be treated, if necessary, with stirring and/or with preheating and mixing them (preferably at an elevated temperature). The stirring and mixing can be performed using a conventional blender, preferably blenders capable of applying a shear force such as Henschel mixer or super mixer. The same solution or dispersion of the coupling agent as used in the wet method can be used in the drying method. The preheating and heating are effected to elevate the temperature to the range which does not cause the decomposition or degradation of the component to be treated.

The surface treatment can also be performed by adding the silane coupling agent or a solution or dispersion thereof when mixing together the components of the gas generating composition.

In any of the foregoing methods, the amount of the coupling agent to be used can be selected from a broad range depending on the type of the coupling agent, the stability, with time, of the component to be treated and other factors. But generally the amount is about 0.01 to about 10 parts by weight, preferably about 0.1 to about 5 parts by weight, per 100 parts by weight of the component to be treated. When a solution or dispersion of the coupling agent is used, the amount of the solution or dispersion to be used is adjusted to give the foregoing proportions.

The chelating agent which can be used in the invention is not critical and can be selected, for example, from a broad range of conventional chelating agents which do not show alkalinity when dissolved or dispersed in water and/or an organic solvent and which can form a chelate in combination with a metal (e.g. Cu, Co, Cr, Ca, etc.) or its ions present in the compound which induces the decomposition of the gas generating base. Examples of useful chelating agents are chelating reagents, photometric reagents, metal indicators, etc.

Examples of chelating reagents which can be used are ethylenediamine-tetraaceic acid (EDTA) and metal salts thereof (EDTA • disodium salt, EDTA • dipotassium salt, EDTA • dilithium salt, EDTA • diammonium salt, etc.), trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid • monohydrate (CyDTA), N,N-bis (2-hydroxyethyl)glycine (DHGE), 1,3-

diamino-2-hydroxypropane-N,N,N'N'-tetraacetic acid (DPTA-OH), diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA), ethylenediamine-N,N'-diacetic acid (EDDA), ethylenediamine-N,N'-dipropionic acid • dihydrochloride (EDDP), ethylenediamine-N,N'-bis(methylenephosphonic acid) • 1/2 hydrate (1/2H_2O)(EDDPO), N-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (EDTA-OH), ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid) (EDTPO), O,O'-bis(2-aminoethyl)ethyleneglycol-N,N,N',N'-tetraacetic acid, N,N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid (HBED), 1,6-hexamethylenediamine-N,N,N',N'-tetracetic acid (HDTA), N-(2-hydroxyethyl)iminodiacetic acid(HIDA), iminodiaceic acid (IDA), 1,2-diaminopropane-N,N,N',N'-tetraacetic acid (methyl-EDTA), nitrilotriacetic acid (NTA), nitrilotripropionic acid (NTP), nitrilotris(methylenephosphonic acid) • trisodium salt (NTPO), triethylenetetramine-N,N,N',N'', N''',N'''-hexaacetic acid (TTHA), etc.

Examples of useful photometric reagents and metal indicators are 3-[N,N-bis(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone, 3,3'-dimethoxybenzine-N,N,N', N'-tetraacetic acid • tetrasodium salt, dimethyldithiocarbamic acid • sodium salt (DDTC), 2,7-bis(2-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalene • disulfonate, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid • disodium salt, 4,7-diphenyl-1,10-phenanthroline, 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione • potassium salt, N-benzoyl-N-phenylhydroxyamine (BPA), N-benzoyl-N-(2-methylphenyl)hydroxyamine (BTA), N-cinnamoyl-N-phenylhydroxylamine (CPA), 5',5''-dibromopyrogallolsulfonphthalein (BPR), 2-hydroxy-1-(1-hydroxy-2-naphthylazo)-6-nitro-4-naphthalenesulfonic acid • sodium salt (BT),3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]fluorescein(calcein)), 8-[N,N-bis(carboxymethyl)aminomethyl]-4-methylumbelliferone(calcein blue), 2,8-dihydroxy-1-(8-hydroxy-3,6-disulfo-1-naphthylazo)-3,6-naphthalenedisulfonic acid • tetrasodium salt, 2-hydroxy-1-(2-hydroxy-5-methylpheylazo)-4-naphthalenesulfonic acid,2-(2-arsonophenylazo)-7-(2-carboxyphenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid, 2,5-dichloro-3,6-dihydroxy-p-benzoquinone, 2,7-bis(4-chloro-2-phosphonophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid, 2,6-dichloro-4'-hydroxy-3',3''-dimethyl-3-sulfofuchsone-5',5''-dicarboxylic acid • trisodium salt, 4,4'-diantipyrylmethane • monohydrate, 1-hydroxy-2-(2-hydroxyphenylazo)benzene,2,7-bis(4-methyl-2-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid, 2,2-bipyridine, 1,2-bis(2-furyl)ethanedione dioxime • monohydrate, 2,2-benzoxazoline, 3,3'-bis[N-(carboxymethyl)aminomethyl]-thymolsulfonphthalein (GTB), 2-hydroxy-1-(2-hydroxy-4-sulfo-1-napthylazo)-3,6-naphthalenedisulfonic acid • trisodium salt, 5-chloro-2-hydroxy-3-(2,4-dihydroxyphenylazo)benzenesulfonic acid, 3, 3'-bis[N,N-bis(carboxymethyl)aminomethyl]-thymolsulfonphthalein • sodium salt, purpuric acid • ammonium salt, 3,3'-[N,N-bis(carboxymethyl)aminomethyl]-p-xylenolsulfonphthalein,2,9-dimethyl-1,10-phenanthroline,2-(2-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid • disodium salt, 2-nitrophenylarsonic acid, 5-nitro-1,10-phenanthroline, 2-nitroso-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol, 2-nitroso-5-[N-ethyl-N-(3-sulfopropyl)amino] phenol, 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid, 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]aniline • sodiumsalt, 1,3-diamino-4-(5-bromo-2-pyridylazo)benzene, 1,8-dihydroxy-2-(2-pyridylazo)-3,6-naphthalenedisulfonic acid • disodium salt, 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol • disodium salt dihydrate, 2-(5-chloro-2-pyridylazo)-5-diethylaminophenol, 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol, 2-(5-nitro-2-pyridylazo-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol • disodium salt • dihydrate, 2-(3,5-dibromo-2-pyridylazo)-5-dimethylaminobenzoic acid, 5-dimethylamino-2-(2-thiazolylazo)benzoic acid, 4-(3,5-dibromo-2-pyridylazo)-N-ethyl-N-(3-sulfopropyl)aniline • monohydrate, 4-methyl-5-(sulfomethylamino)-2-(2-thiazolylazo)benzoic acid, 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo)resorcinol, 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolphthalein, 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine, 3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2-4-triazine • disodium salt, 1,10-phenanthroline • monohydrate,3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]phenolphthalein, 5,10, 15, 20-tetrakis(N-methylpyridinium-4-yl)-21H, 23H-porphyrin and tetrakis thereof(p-toluene sulfonate), 5, 10, 15, 20-tetraphenyl-21H, 23H-porphyrin, 5, 10, 15, 20-tetraphenyl-21H, 23H-porphyrin tetrasulfonic acid • disulfuric acid tetrahydrate, 5, 10, 15, 20-tetrakis{4-[N-(trimethyl)ammonio]phenyl}-21H, 23H-porphyrin and tetrakis thereof(p-toluene sulfonate), synphenyl-2-pyridylketoxime, pyrogallolsulfophthalein, pyrocatechol, sulfophthalein, N,N,'-bissalicylidene-2,3-diaminobenzofuran, salicylaldehyde-2-oxyanile, 3,3'-bis{[N-methyl-N-(carboxymethyl)]aminomethyl}-o-cresolsulfophthalein • monosodium salt, 4,4'-dicarboxy-2,2'-biquinoline • disodium salt, 4,4'-bis(3,4-dihydroxyphenylazo)-2,2'-stilbenedisufonate • diammonium salt, 4,4'-diamino-2,2'-disulfostilbene-N,N,N',N'-tetraacetic acid • disodium salt, 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-butene-2-one, 4-{2-arsono-4-nitrophenylazo)amino]phenylazo}benzenesulfonic acid • monosodium salt, 1,8-dihydroxy-2,7-bis(5-chloro-2-hydroxy-3-sulfophenylazo)-3,6-naphthalenedisulfonicacid • tetrasodium salt, 1,8-dihydroxy-2,7-bis(2-sulfophenylazo)-3,6-napthalenedisulfonic acid • tetrasodium salt, 4-methyl-2-(2-thiazolylazo)phenol, 5-dimethylamino-2-(2-thiazolylazo)phenol, 1-(2-thiazolylazo)-2-naphthol, 4-(2-thiazolylazo)resorcinol, 3'-nitro-4'-(2,4,6-trinitrophenylamino)benzo-18-crown-6, N,N',N'',N'''-tetramethylpurpuric acid • ammonium salt, 4'-(2,4-dinitro-6-trifluoromethylphenyl)aminobenzo-15-crown-5,8- mercaptoquinoline • hydrochloride, 1,2-dihydroxy-3,5-benzenesulfonic acid • disodium salt monohydrate, 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]thymolphthalein, 2,4,6-tris(2-pyridyl)-1,3,5-triazine, N-(4-methoxyphenyl)-1,4-phenylenediamine • hydrochloride, 2-[3-(2,4-dimethylphenylaminocarboxy)-2-hydroxy-1-naphthylazo]phenol, 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolsulfonphthalein, 2-[1-(2-hydroxy-5-sulfophenyl)-3-phenyl-5-formazano]benzoic acid • monosodium salt, 1,2-dimercaptosuccinic acid, N-(dithiocarboxy)sarcosine • diammonium salt, tetraphenylborate • sodium salt, 3-mercaptopropionic acid, phenylarsonic acid, tetraphenylphosphonium chloride, etc.

Among the above examples of chelating agents, the chelating reagent is preferred and EDTA • disodium salt is more preferred.

The above-exemplified chelating agents can be used either alone or in combination.

The surface treatment using a chelating agent can be done by conventional methods. Stated more specifically, a chelating agent is dissolved or dispersed in a suitable solvent, and the solution or dispersion is mixed with the compound to be surface-treated. While water is chiefly used as the solvent, some chelating agents are sparingly soluble in water. When such chelating agent is used, a suitable organic solvent is used as selected from, e.g. methanol, ethanol, isopropanol, n-amyl alcohol, methyl isobutyl ketone, chloroform, carbon tetrachloride, benzene, nitrobenzene, triethanolamine, etc. The amount of the chelating agent to be used is suitably selected from a broad range depending on the type of the chelating agent, the type of the compound to be surface-treated, etc. The concentration and the amount of the chelating agent are adjusted to use about 10 to about 200 parts by weight, preferably about 50 to about 150 parts by weight of the chelating agent, per 100 parts by weight of the compound to be surface-treated. The mixing time is suitably selected and is usually about 0.5 to about 4 hours. The surface treatment is carried out if necessary with heating, e.g. at a temperature of about 50 to about 80°C.

The air bag gas generating composition of the present invention can be prepared by mixing together the three essential components and other components to be optionally used. Further the air bag gas generating composition of the present invention can be molded into a suitable shape. For example, a suitable amount of a binder is admixed with the gas generating composition of the invention and the mixture is tabletted and, if necessary, dried. In this case, preferably a solvent such as water is added in a proper amount to assure safety. Useful binders include, for example, those usually used for this purpose. The shape of the discrete preparation is not critical and includes, for example, a pellet, disk, ball, bar, hollow cylinder, confetti and tetrapod. It may be solid or porous (e.g. honeycomb-shaped). One or more projections may be formed on one or both surfaces of pellets or disks. The shape of projections is not critical and includes, for example, cylinders, cones, polygonal cones, polygonal pillars, etc. Further, the size of tablets formed from the gas generating composition of the invention is not specifically limited and can be suitably selected from a broad range. However, a suitable size of tablets is about 0.3 to about 1.5 mm in diameter from the standpoints of obtaining a lower burning temperature and a more suitable burning velocity.

Optionally the respective components may be individually tabletted and the tablets may be used as mixed.

The tabletted gas generating preparation of the invention is placed into a container made of polyethylene or like synthetic resins or metals, whereby the gas generating preparation can be safely stored and transported.

Next, the air bag inflator of the present invention is described below. The feature of the air bag inflator of the invention is that an oxidizer for external use is disposed on at least one part of a passage for passing the after gas into the air bag. Consequently the inflator is not specifically limited, and inflators having a known structure can be widely used.

Oxidizers to be externally used in the invention can be the same conventional oxidizers as used in the gas generating composition of the invention or can be other conventional species.

The part of the inflator for disposing the oxidizer for external use is not specifically limited insofar as it is on a passage for the after gas to pass therethrough but not on the combustion chamber. For example, the external oxidizer may be placed on a coolant, a wire netting filter, a ceramic filter, etc. The number of inflator parts on which the external oxidizer is placed is not necessarily limited to one and may be two or more.

According to the present invention, the external oxidizer is decomposed due to the high temperature of a gas evolved on combustion of the gas generating composition, whereby oxygen is produced and the cobalt and the like in the gas are oxidized, further reducing the CO concentration. Consequently it is desirable that the gas coming into contact with the external oxidizer be heated to a high temperature. Stated more specifically, the external oxidizer is preferably placed on a coolant with which the gas released from the combustion chamber is first brought into contact.

The external oxidizer can be mounted on the desired inflator component, for example, by immersing a coolant, a wire netting filter, a ceramic filter or the like in an aqueous solution or dispersion, or an organic solvent solution or dispersion, of the external oxidizer, followed by drying. Stated more specifically, an aqueous solution or dispersion, or an organic solvent solution or dispersion, of the external oxidizer is heated to a temperature of about 70 to about 100°C, and the inflator component is dipped into the heated solution or dispersion, which is then cooled, whereby an oxidizer layer is deposited on the surface of the inflator component. Thereafter the component is withdrawn and dried.

Optionally, the external oxidizer may be placed on an inflator component by spraying the inflator component with a solution or dispersion of the external oxidizer and drying the coated component.

Further optionally, the external oxidizer molded in the shape of a pellet or disk may be disposed on at least one part of the passage for the release of the gas.

While there is no specific restriction on the air bag gas generating compositions to be charged into the combustion chamber of the air bag inflator of the present invention, an azide-free gas generating composition is preferred, and the gas generating composition of the present invention is more preferred. When the gas generating composition is placed into the combustion chamber, at least one species selected from oxidizers, gas-releasing inorganic compounds and inert inorganic compounds may be accommodated together into the combustion chamber. These three types of components are hereinafter referred to as "prooxidant for combustion chamber" for the sake of expedience.

Oxidizers to be used among the prooxidants for combustion chamber can be any of those exemplified above. Of these examples, potassium nitrate and like nitrates, and sodium chlorate and like oxyhalogen acid salts are preferred. Useful gas releasing inorganic compounds include a wide range of known compounds capable of generating a gas on thermal decomposition, e.g. sodium bicarbonate. Useful inert inorganic compounds include a wide range of known compounds free of thermal decomposition, e.g. silicon dioxide.

Of the above examples of the prooxidants for combustion chamber, potassium nitrate, sodium chlorate and like oxidizers, silicon dioxide and like inert inorganic compounds overlap some of the components for the gas generating composition of the invention. However, if these compounds are incorporated into the gas generating composition in the combined amount of the compound as the component of the gas generating composition and the compound as the prooxidant for combustion chamber, a proper burning velocity can not be attained and accordingly the CO concentration can not be lowered.

There is no specific limitation on the shape of the prooxidant for combustion chamber. The prooxidant for combustion chamber can be used as a powder or as molded into any desired form selected from a pellet, disk, precipitate, granule, etc.

When the prooxidant for combustion chamber is charged into the combustion chamber together with the gas generating composition of the invention, a partition means may be provided between them to separate them, such as a thin sheet of aluminum, aluminum foil, etc.

The air bag gas generating composition of the invention and the air bag inflator of the invention are not limited to automotive use and can be suitably used as a gas source for air bag systems to be installed in various transport means.

According to the present invention, when a specific burning catalyst is incorporated into an azide-free air bag gas generating composition containing a nitrogen-containing organic compound as a gas generating bas, the azide-free air bag gas generating composition becomes capable of further reducing the concentrations of CO and other toxic components in the after gas while maintaining the above-mentioned desired advantages of azide-free gas generating compositions such as adequate burning velocity, amount of generated gas and gas temperature which are superior or equivalent to those of conventional azide-based gas generating compositions, lower impact ignitability than azide-based gas generating compositions, high safety, low toxicity and low costs. According to the present invention, there is also provided an air bag inflator capable of further reducing the concentrations of CO and other components in the after gas. The present invention further provides a method of overcoming the drawback of the azide-free gas generating composition that the nitrogen-containing organic compound such as azodicarbonamide in the composition decomposes during a long term storage after production, stated more specifically the method comprising surface treatment with a coupling agent or a chelating agent.

Brief Description of the Drawings

FIG. 1 schematically shows a device to be used in a burning test for testing the gas generating compositions obtained in Examples to be described later.

FIG. 2 is a diagrammatic section view showing an example of the inflator of the invention.

Best Mode of Carrying Out the Invention

The present invention is described below in more detail with reference to the following Examples, Comparative Examples and Reference Examples.

The manufacturers of conventional starting materials used below are as follows unless otherwise specified.

Azodicarbonamide:	product of Otsuka Kagaku Kabushiki Kaisha
Potassium nitrate:	product of Otsuka Kagaku Kabushiki Kaisha
Potassium perchlorate:	product of Nihon Carlit Co., Ltd.
Silicon dioxide:	trademark "Tockseal N", product of Tokuyama Soda Co., Ltd.
Soluble starch:	Wako 1st grade product, product of Wako Junyaku Co., Ltd.

The parts and percentages in the following description are all by weight.

Example 1

Mixed well were powders of 45 parts of azodicarbonamide, 55 parts of potassium perchlorate, 10 parts of copper oxide (specific surface area 48 m^2/g, average particle size about 7.4 μm, product of Nikki Kagaku K.K.) and 1.1 parts of silicon dioxide. A 10% aqueous solution of soluble starch was added in an amount sufficient to provide a starch content of 1.5 parts, and mixed, thereby giving a wet powder. The wet powder was granulated by a granulator. The obtained wet granules were dried. Using a hydraulic tablet molding machine, the dried granules were compressed to give pellets

of a gas generating composition (6 mm in diameter, 3 mm thick, 0.15 g in weight).

A 30 g quantity of the obtained pellets of the gas generating composition was charged into the combustion chamber of an inflator having a gas vent 6 mm in diameter wherein 0.8 g of boron/potassium nitrate was placed as a transfer charge. The inflator was set in a 60-liter tank and operated by passing an electric current. Thereafter the gas in the tank was collected through a gas outlet in the tank into a 1-liter tedlar bag. The CO concentration in the collected gas was 0.8% when measured using a detecting tube.

Comparative Example 1

Pellets of a gas generating composition were produced in the same manner as in Example 1 with the exception of using copper oxide (specific surface area 0.77 m^2/g, average particle size about 4.5 μm) conventionally used for gas generating compositions.

Using the obtained pellets of the gas generating composition, the same procedure as in Example 1 was repeated. The CO concentration in the gas was 1.5%.

The above result shows that the incorporation of CuO having a large specific surface area produced a marked effect in the reduction of CO concentration in the gas.

Example 2

Mixed well were powders of 45 parts of azodicarbonamide, 55 parts of potassium perchlorate, 10 parts of each burning catalyst having the composition as shown below in Table 1, 1.1 parts of silicon dioxide and 0.55 part of soluble starch. A 0.2 g quantity of the powders was packed into the cavity of a mold 6 mm in diameter and compressed under a pressure of 40 kgf/cm^2 using a manual-type hydraulic press, giving pellets of gas generating compositions according to the invention (6 mm in diameter, 0.2 g in weight).

Table 1

No.	CuO	Cr_2O_3	Mn_2O_3	Specific surface area
1	40	40	20	54 m^2/g
2	43	53	4	53 m^2/g
3	100	-	-	48 m^2/g

The catalysts Nos. 1 to 3 are all products of Nikki Kagaku K.K.

The gas generating compositions thus obtained were subjected to a burning test using the burning tester shown in FIG. 1.

(1) Placing pellets of the gas generating composition onto nichrome wire, the tester was constructed as shown in the drawing.
(2) The air in the tedlar bag and the test tube was replaced by a helium gas (300 ml/min, 10 minutes).
(3) The tedlar bag was pressed to discharge the helium gas into the test tube and the cock of the bag was closed (not shown).
(4) The helium gas remaining in the tedlar bag was withdrawn by a gas syringe (not shown).
(5) The test glass tube was closed and the 3-way cock was adjusted to release a gas evolved by combustion into the tedlar bag.
(6) The supply of helium gas was stopped and the cock of the bag was opened.
(7) An ignition bus bar was connected to the nichrome wire and the pellets of the gas generating composition were ignited using a slide auto-transformer (not shown) and burnt.
(8) The gas discharged into the tedlar bag was analyzed by gas chromatography.
(9) The amount of the gas in the tedlar bag was measured by a gas syringe.

The results are shown in Table 2.

Comparative Example 2

The same procedure as in Example 2 was repeated with the exception of using copper oxide alone as a burning

catalyst which was conventionally employed for gas generating compositions (specific surface area 0.77 m^2/g, average particle size about 4.5 μm), giving pellets of a gas generating composition.

The obtained pellets were subjected to the same burning test as in Example 2, and only the CO concentration was measured. The results are shown in Table 2.

Table 2

Gas concentration	Example 2			Compar. Example 2
	No.1	No.2	No.3	
O_2 %	2.5	1.2	7.1	16.7
N_2 %	25.5	26.4	21.1	27.3
CO %	2.4	1.4	2.1	4.8
CO_2 %	23.3	26.5	18.7	16.0
Gas amount (ml)	94.2	93.2	111.2	93.2

Table 2 shows that when the burning catalysts of the invention were used together with other oxidizers, a remarkable effect was produced in reducing the CO concentration.

Example 3

The procedure of Example 1 was repeated with the exception of using the burning catalyst No.2 of Example 2, increasing the content of potassium perchlorate to 5, 10 or 15% and using the soluble starch in an amount of 0.55 part, giving pellets of gas generating compositions according to the invention.

The obtained pellets were subjected to the same burning test as in Example 2. The results are shown in Table 3.

Table 3

Increase of potassium perchlorate (%)	5%	10%	15%
Gas concentration			
O_2 (%)	2.6	4.3	5.2
N_2 (%)	28.6	21.6	23.8
CO (%)	1.6	1.1	1.0
CO_2 (%)	27.7	26.4	26.9
Gas amount (ml)	0.32	103.2	97.2

Table 3 shows that slight increases in the amount of potassium perchlorate further reduced the CO concentration.

Example 4

Mixed well were powders of 45 parts of azodicarbonamide, 56.3 parts of potassium perchlorate, 10 parts of potassium nitrate, 1 part of silicon dioxide and a molybdenum oxide in the amount (part) shown in Table 4. Added thereto was a 10% aqueous solution of soluble starch in an amount sufficient to provide a starch content of 1.5 parts, followed by mixing, producing a wet powder. The same subsequent procedure as in Example 1 was conducted, giving 9 types of pellets of gas generating compositions (6 mm in diameter, 3 mm thick, 0.15 g in weight).

Table 4

Sample No.	Burning catalyst	Amount
1	Molybdenum oxide (VI)	0.25
2	Molybdenum oxide (VI)	0.5
3	Molybdenum oxide (VI)	1.0
4	Molybdenum oxide (VI)	2.0
5	Molybdenum oxide (VI)	4.0
6	Molybdenum oxide (VI)	5.0
7	Molybdenum oxide (VI)	6.0
8	Nickel molybdate	5.0
9	Cobalt molybdate	5.0

Comparative Example 3

Mixed well were powders of 45 parts of azodicarbonamide, 55 parts of potassium perchlorate, 10 parts of copper oxide (specific surface area 0.77 m^2/g, average particle size about 4.5 μm) conventionally employed for gas generating compositions and 1 part of silicon dioxide. Added thereto was a 10% aqueous solution of soluble starch in an amount sufficient to give a starch content of 1.0 part, followed by mixing, thereby producing a wet powder. The same subsequent procedure as in Example 1 was carried out, giving pellets of a gas generating composition (No.1).

The same procedure as above was repeated with the exception of altering the amount of potassium perchlorate to 65 parts and the amount of copper oxide to 20 parts, giving pellets of a gas generating composition (Sample No.2).

The pellets of the gas generating compositions obtained above were subjected to a 60-liter tank test described below.

[60-liter tank test]

Each of 11 types of pellets of the gas generating compositions prepared in Example 4 and Comparative Example 3 was placed into the combustion chamber of an inflator having a gas vent 7 mm in diameter and loaded with 0.8 g of boron/potassium nitrate as a transfer charge. The inflator was set in a 60-liter tank and operated by passing a current to ignite the pellets of the gas generating composition. Then the pressure and the temperature in the inflator and in the 60-liter tank were measured. A gas evolved by combustion in the 60-liter tank was collected through a gas outlet into a 1-liter tedlar bag, and the concentrations of CO and NO_x in the gas were determined using a detecting tube. The results are shown in Table 5.

The symbols in Table 5 stand for the following.

CPmax: Maximum pressure (kgf/cm^2) in the combustion chamber of the inflator

TPmax: Maximum pressure (kgf/cm^2) in the 60-liter tank (a parameter showing the gas generating capability of the gas generating composition)

tTPmax: Time taken (msec) until the maximum pressure is reached in the 60-liter tank (a parameter simulating the gas temperature in the air bag when the air bag has become fully inflated)

tTP90: Time taken (msec) until the maximum pressure (90%) is reached in the 60-liter tank (a parameter simulating the gas temperature in the air bag when the air bag has become fully inflated)

Table 5

Sample No.	Amount (g)	CPmax	TPmax	tTPmax	tTP90	Ttemp. (°C)	CO (%)	NO_x (ppm)
		(kgf/cm^2)		(msec)				
1	35	92	0.7	35	20	41	1.20	1200
2	35	100	1.1	29	20	67	0.96	1500
3	30	44	0.5	580	-	39	0.96	1300
4	30	122	0.5	27	17	49	0.82	1100
5	30	102	0.6	140	-	42	0.90	1300
6	20	80	0.3	-	-	34	0.45	750
6	30	190	1.0	42	22	61	0.42	1100
7	30	62	0.7	250	170	34	0.65	1600
8	40	94	1.2	80	-	75	0.49	2300
9	30	44	0.7	140	-	47	0.67	2150
1	30	90	1.4	57	-	-	1.35	800
2	30	74	1.24	96	-	-	0.32	1800

Note: Samples Nos. 1 to 9 were prepared in the Example, while Samples Nos. 1 and 2 in the lower rows were prepared in the Comparative Example.

Table 5 shows the following. (1) The air bag gas generating compositions of the present invention can generate a suitable amount of gas and have a good combustibility. (2) The air bag gas generating compositions of the present invention containing molybdenum oxide (VI) can reduce the concentrations of CO and NO_x due to the presence of the oxide at the same time to an extent equivalent to or greater than that attained in Comparative Example 3 wherein copper oxide was used. (3) Apparently the formulation of Sample No.6 in Example 4 can significantly reduce the concentrations of CO and NO_x.

Nine kinds of pellets of the gas generating compositions prepared in Example 4 were all 99.5% or more in the residual rate (%, by weight) as measured after 400-hour storage in a thermostatic container at 107°C. The data indicate that the decomposition of the azodicarbonamide substantially did not occur.

On the other hand, the same procedure as above was repeated with the exception of using 2 types of pellets of the gas generating compositions prepared in Comparative Example 3 and storing them for 190 hours. The residual rates (%, by weight) were 72% (No.1) and 68% (No.2). It is clear that the azodicarbonamide pronouncedly decomposed.

Example 5

Mixed well were powders of 45 parts of azodicarbonamide, 65 parts of potassium perchlorate, 1 part of silicon dioxide and tungsten oxide (No.1) in the amount (part) shown in Table 6. Added thereto was a 10% aqueous solution of soluble starch in an amount sufficient to provide a starch content of 1.5 parts, followed by mixing, thereby producing a wet powder. The same subsequent procedure as in Example 1 was conducted, giving pellets of a gas generating composition (6 mm in diameter, 3 mm thick, 0.15 g in weight).

The same procedure as above was repeated with the exception of altering the amount of potassium perchlorate to 56.3 parts, using tungsten oxides Nos. 2-8 shown in Table 6 and adding 10 parts by weight of potassium nitrate, giving pellets of gas generating compositions (6 mm in diameter, 3 mm thick, 0.15 g in weight).

Table 6

No.	Burning catalyst	Amount
1	$CoWO_4$	10
2	$NiWO_4$	10
3	$FeWO_4$	5
4	WO_3	5
5	WO_3	10
6	WO_3	15
7	WO_3	2
8	WO_3	1

Using the pellets of the gas generating compositions prepared in Example 5, a 60-liter tank test was carried out to measure the pressure and the temperature in the inflator and the 60-liter tank and the CO and NO_x concentrations in the after gas. The results are shown in Table 7. The amount of the pellets respectively charged was 40 g.

Table 7

Sample No.	CPmax	TPmax	tTPmax	tTP90	Ttemp. (°C)	CO (%)	NO_x (ppm)
	(kgf/cm^2)		(msec)				
1	112	1.3	28	17	96	0.36	1730
2	122	1.2	25	17	115	0.75	1400
3	112	0.9	29	16	89	0.68	1200
4	98	0.8	33	19	77	0.68	1200
5	102	1.1	344	35	108	0.53	1450
6	64	0.8	632	320	80	0.47	1350
7	88	0.9	39	23	74	0.65	1000
8	50	0.7	2060	-	72	0.49	800

Eight kinds of pellets of the gas generating compositions prepared in Example 5 were all at least 99.5% in residual rate (%, by weight) as measured after 400-hour storage in a thermostatic container at 107°C. The data show that substantially no azodicarbonamide decomposed.

Example 6

(1) Pellets of the gas generating composition of Comparative Example 1: 30 g
(2) Prooxidant for combustion chamber (sodium chlorate): 10 g
(3) Transfer charge (boron/potassium nitrate): 0.8 g

The pellets of the gas generating composition were placed into the combustion chamber of an inflator having a gas vent 6 mm in diameter, aluminum foil of 15 μm thickness was disposed on the pellets, and then sodium chlorate was charged into the combustion chamber.

The inflator was set in a 60-liter tank and a current was passed to ignite the pellets of the gas generating composition. Then the pressure in the combustion chamber and in the tank pressure was measured. A gas evolved by combustion in the tank was collected through a gas outlet into a 1-liter tedlar bag. Using a detecting tube, the collected gas was analyzed, and the CO concentration was 0.95%. The maximum combustion chamber pressure was 109 kgf/cm^2, and

the maximum tank pressure was 0.7 kgf/cm^2.

It is clear that the CO concentration was further reduced as compared with the value of Comparative Example 1 (CO concentration 1.5%).

Example 7

The procedure of Example 6 was repeated with the exception of using potassium nitrate in place of sodium chlorate as a prooxidant for combustion chamber. The CO concentration in the after gas was 1.0%, while the maximum combustion chamber pressure was 82 kgf/cm^2, and the maximum tank pressure was 0.8 kgf/cm^2.

Examples 8 and 9

A burning test was performed using the pellets of the gas generating composition prepared in Comparative Example 1 and potassium nitrate as a prooxidant for combustion chamber in the amounts (part) shown in Table 8. Potassium nitrate was placed into the combustion chamber of an inflator having a gas vent 7 mm in diameter. Thereafter aluminum foil of 15 μm thickness was disposed on the potassium nitrate and the pellets of the gas generating composition were deposited on the aluminum foil.

The inflator was set in a 60-liter tank and the same procedure as in Example 6 was repeated. The results are shown in Table 8.

Comparative Example 4

The same procedure as in Examples 8 and 9 was repeated with the exception of not using potassium nitrate as the prooxidant for combustion chamber. The results are shown in Table 8.

Table 8

	Ex. 8	Ex. 9	Com.Ex.4
Pellets of gas generating composition	20	25	20
Prooxidant for combustion chamber (potassium nitrate)	10	15	-
CO concentration (%)	0.8	0.8	1.1
Maximum combustion chamber pressure (kgf/cm^2)	44	56	72
Maximum tank pressure (kgf/cm^2)	0.4	0.7	0.6

Table 8 shows that the addition of the prooxidant for combustion chamber lowered the combustion chamber pressure and reduced the CO concentration in the after gas.

Example 10

FIG. 2 is a diagrammatic section view of an example of the inflator according to the present invention. The inflator is basically provided with a combustion chamber 1, a gas generating composition 2, a squib 3, a transfer charge 4, a gas vent 5, a coolant 6, a wire netting filter 7 and a ceramic filter 8, and has the same structure as conventional inflators except that an external oxidizer is present on the coolant 6 (not shown).

The squib 3 comprises a lead wire 9, a platinum electrode (not shown) and a sensitizer 10.

The mechanism for the generation of a gas is as follows. An electric current was passed through the lead wire 9, thereby heating the platinum electrode. Then the sensitizer 10 was electrically ignited by the heat to ignite the transfer charge 4. The ignited transfer charge 4 burned the gas generating composition 2, which then emitted a gas. The high temperature gas just generated was led to the coolant 6 via the gas vent 5, and was cooled. The CO component in the gas was oxidized to carbon dioxide by oxygen evolved on thermal decomposition of an external oxidizer disposed on the coolant 6, whereby the CO concentration was reduced. The gas flowing through the coolant 6 was passed through the wire netting filter 7 and then through the ceramic filter 8 and the filter 7 to thereby remove the solid impurities. Then the gas was finally discharged into an air bag (not shown) via an exhaust port.

The external oxidizer was disposed on the coolant 6 as follows. The coolant 6 was dipped into a saturated aqueous solution of sodium chlorate heated to 100°C. Subsequently the aqueous solution was cooled to deposit a layer of sodium chlorate on the surface of the coolant 6. Thereafter the coolant 6 with the sodium chlorate layer thereon was

withdrawn from the solution and dried by heating. A wire netting of copper weighing 10 g was used as the coolant 6, and the amount of sodium chlorate deposited on the coolant 6 was 22 g.

Example 11

Into the inflator of the present invention shown in FIG. 2 were placed 30 g of the pellets of the gas generating composition of Comparison Example 1, a squib (product of Daicel Chemical Industries, Ltd.) and 0.8 g of transfer charge (boron/potassium nitrate). In the inflator of the invention, sodium chlorate was disposed as an external oxidizer on the coolant. The amount of the deposit is shown in Table 9.

The inflator was set in a 60-liter tank and operated by passing a current. Then the internal pressure in the inflator and the internal pressure in the tank were measured. After said procedure, a gas evolved in the tank was collected through a gas outlet into a 1-liter tedlar bag. The CO concentration of the gas collected in the tedlar bag was measured using a detecting tube. The results are shown in Table 9.

Table 9

No.	Amount of deposit	CO concentration
1	5 g	1.0%
2	10 g	0.8%
3	18 g	0.6%

It is clear that the CO concentration was further reduced owing to the sodium chlorate deposited as an external oxidizer on the coolant as compared with the CO concentration (1.5%) in Comparative Example 1.

Example 12

A 60-liter tank test was conducted in the same manner as in Example 11 with the exception of using potassium chlorate (deposition amount 10 g) in place of sodium chlorate used as an external oxidizer in Example 11 with the result that the CO concentration in the after gas was 0.8%.

Example 13

A 60-liter tank test was conducted in the same manner as in Example 11 with the exception of altering the amount of the pellets of the gas generating composition to 35 g and using potassium nitrate (deposition amount 20 g) in place of sodium chlorate as an external oxidizer with the result that the CO concentration in the after gas was 0.5%.

Reference Example 1

Ten parts of a 1% methanol solution of γ-aminopropyltriethoxysilane (trade name: "A-1100, product of Nihon Unika K.K.) was added to 100 parts of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.). Using a super mixer (product of Kawada Seisakusho K.K.), the two components were mixed at 40°C and 600 rpm for 5 minutes and dried, giving a surface-treated copper oxide.

Reference Example 2

A surface-treated copper oxide was produced in the same manner as in Reference Example 1 with the exception of using γ-glycidyloxypropyltrimethoxysilane (trade name: A-187, product of Nihon Unika K.K.) in place of γ-aminopropyltriethoxysilane.

Reference Example 3

Ten parts of a 3% hexane solution of isopropyl triisostearoyl titanate (trade name "Planeact KR-TTS", product of Ajinomoto Co., Inc.) was added to 100 parts of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.). The two components were mixed and dried in the same manner as in Reference Example 1, producing a surface-treated copper oxide.

Reference Example 4

Ten parts of a 2% hexane solution of acetoalkoxyaluminum diisopropyrate (trade name "Planeact AL-M", product of Ajinomoto Co., Inc.) was added to 100 parts of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.). The two components were mixed and dried in the same manner as in Reference Example 1, producing a surface-treated copper oxide.

Reference Example 5

Ten parts of a 0.5% toluene solution of acetoalkoxyaluminum diisopropyrate (trade name "Alumichelate A", product of Kawaken Fine Chemical Co., Ltd.) was added to 100 parts of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.). The same subsequent procedure as in Reference Example 1 was repeated for mixing and drying, producing a surface-treated copper oxide.

Examples 14 to 18

Mixed well were powders of 45 parts of azodicarbonamide, 55 parts of potassium perchlorate, 10 parts of each of the surface-treated copper oxides produced in Reference Examples 1 to 5, and 1.0 part of silicon dioxide. Added thereto was a 5% aqueous solution of soluble starch in an amount sufficient to provide a starch content of 1.5 parts, followed by mixing, thereby producing a wet powder. The particle size and the water content of the powder were adjusted. Thereafter the powder was compressed under a pressure of 120 kg/cm^2 by a hydraulic tablet molding machine, giving pellets of gas generating compositions (9.7 mm in diameter, 4 mm thick).

Comparative Example 5

Pellets of a gas generating composition were prepared in the same manner as in the above examples with the exception of using copper oxide having an untreated surface.

The air bag gas generating compositions prepared in Examples 14 to 18 and Comparative Example 5 were stored in a thermostatic container at 107°C for 400 hours. The residual rate (%) of the azodicarbonamide was calculated based on the decrease in the weight. The results are shown below in Table 10.

Table 10

	Copper oxide	Residual rate (%)
Example 14	Reference Ex. 1	96
Example 15	Reference Ex. 2	94
Example 16	Reference Ex. 3	95
Example 17	Reference Ex. 4	97
Example 18	Reference Ex. 5	97
Comp. Ex. 5	Untreated	60

Table 10 shows that the stability of azodicarbonamide was remarkably improved by surface-treating the copper oxide with the coupling agent. The gas generating compositions of Examples 14 to 18 retained the desired advantages of azide-free gas generating compositions such as suitable burning velocity, suitable amount of generated gas, low burning temperature, low impact ignitability, high safety, low toxicity, low costs, etc.

Reference Example 6

A 10% aqueous solution of calcium peroxide and a 10% aqueous solution of methyltrimethoxysilane were mixed in equal amounts. The mixture was stirred at about 80°C for 2 hours, and the solids were separated by filtration, washed with water and dried, giving a surface-treated calcium peroxide.

Example 19

Pellets of a gas generating composition were produced in the same manner as in Example 14 with the exception of using the surface-treated calcium peroxide produced in Reference Example 6 in place of the surface-treated copper oxide.

The obtained gas generating composition was stored in the same manner as above in a thermostatic container at 107°C for 400 hours. The residual rate (%) of the azodicarbonamide was 99.5% when measured based on the decrease in the weight. Apparently the decomposition was markedly inhibited due to the surface treatment.

Comparative Example 7

The procedure of Example 19 was repeated with the exception of using an untreated calcium peroxide, producing pellets of a gas generating composition. The azodicarbonamide of the obtained pellets was completely decomposed on addition of an aqueous solution of soluble starch before a 400-hour storage test was conducted at 107°C.

The above results show that the surface treatment of calcium peroxide with a coupling agent pronouncedly enhances the stability of dicarbonamide as a gas generating base.

Reference Example 7

Ten grams of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.) was added to 100 ml of a 10% aqueous solution of EDTA・disodium salt. The two components were mixed with stirring for 1 hour, and the copper oxide was separated by filtration and dried, giving a surface-treated copper oxide.

Reference Example 8

Eighty grams of copper oxide having a specific surface area of 50 m^2/g (product of Nikki Kagaku K.K.) was added to 50 ml of a 10% aqueous solution of sodium diethyldithiocarbamate (DDTC). The two components were mixed with stirring for 2 hours, and the copper oxide was separated by filtration and dried, giving a surface-treated copper oxide.

Reference Example 9

The procedure of Reference Example 7 was repeated with the exception of using chromium oxide (Cr_2O_3) or manganese oxide (Mn_2O_3) in place of copper oxide, giving a surface-treated chromium oxide or manganese oxide.

Examples 20 to 24

Mixed well were powders of azodicarbonamide (ADCA), potassium perchlorate, potassium nitrate, surface-treated metallic oxides produced in Reference Examples 7 to 9, and silicon dioxide. Added thereto was a 5% aqueous solution of soluble starch in an amount sufficient to provide a starch content of 1.5 parts, followed by mixing, thereby producing a wet powder. In Example 20, the surface-treated copper oxide prepared in Reference Example 8 was used. In Examples 21 and 22, the surface-treated copper oxide prepared in Reference Example 7 was used. The particle size and the water content of the obtained wet powder were adjusted. Using a hydraulic tablet molding machine, the powder was compressed under a pressure of about 120 kg/cm^2, giving pellets of gas generating compositions (9.7 mm in diameter, 4 mm thick).

Comparative Example 8

The procedure of Example 20 was repeated with the exception of using an untreated copper oxide, producing pellets of a gas generating composition.

The gas generating compositions prepared in Examples 20 to 24 and Comparative Example 8 were stored in a thermostatic container at 107°C for 400 hours. The residual rate (%) of the azodicarbonamide was calculated based on the decrease in the weight. The results are shown in Table 11 together with other data.

Table 11

	Example					Comp. Example 8
	20	21	22	23	24	
ADCA	45	45	45	45	45	45
$KClO_4$	55	55	55	55	55	55
KNO_3	-	-	10	-	-	-
Metallic oxide						
Surface-treated copper oxide	10	10	10	-	-	-
Surface-treated chromium oxide	-	-	-	10	-	-
Surface-treated manganese oxide	-	-	-	-	10	-
Untreated copper oxide	-	-	-	-	-	10
Silicon dioxide	1	1	1	1	1	1
Residual rate (%)	97	98	98	99	99	60

Table 11 shows that the surface treatment of metallic oxides with the chelating agent markedly increased the stability of azodicarbonamide. The gas generating compositions of Examples 20 to 24 retained the desired advantages of azide-free gas generating compositions such as adequate burning velocity, adequate amount of generated gas, low burning temperature, low impact ignitability, high safety, low toxicity and low costs.

Claims

1. An air bag aside-free gas generating composition comprising a nitrogen-containing organic compound and an oxidizing agent as active components, and further containing, as a burning catalyst, at least one metallic oxide selected from the group consisting of molybdenum oxides, tungsten oxides and metallic oxides having a BET specific surface area of at least 5 m^2/g.

2. The air bag gas generating composition according to claim 1, wherein the nitrogen-containing organic compound is at least one member selected from the group consisting of amino group-containing organic compounds, nitramine group-containing organic compounds and nitrosoamine group-containing organic compounds.

3. The air bag gas generating composition according to claim 1, wherein the nitrogen-containing organic compound is azodicarbonamide.

4. The air bag gas generating composition according to claim 1, wherein the oxidizing agent is at least one member selected from the group consisting of oxyhalogen acid salts, nitrates and nitrites.

5. The air bag gas generating composition according to claim 1, wherein the oxidizing agent consists of oxyhalogen acid salt and nitrate.

6. The air bag gas generating composition according to claim 1, wherein the nitrogen-containing organic compound and/or the compound which induces the decomposition of the nitrogen-containing organic compound is surface-treated with a coupling agent and/or a chelating agent.

7. An air bag inflator wherein an air bag gas generating composition is held in a combustion chamber and wherein an oxidizing agent for external use is disposed on at least one part of a passage for releasing into an air bag a gas evolved by combustion of the gas generating composition.

8. The air bag inflator according to claim 7, wherein the air bag gas generating composition is an azide-free gas generating composition.

9. The air bag inflator according to claim 7, wherein a prooxidant for combustion chamber is charged into the inflator together with the air bag gas generating composition.

10. The air bag inflator according to claim 7, wherein the external oxidizer is disposed on the coolant and/or the filter.

F I G. 1

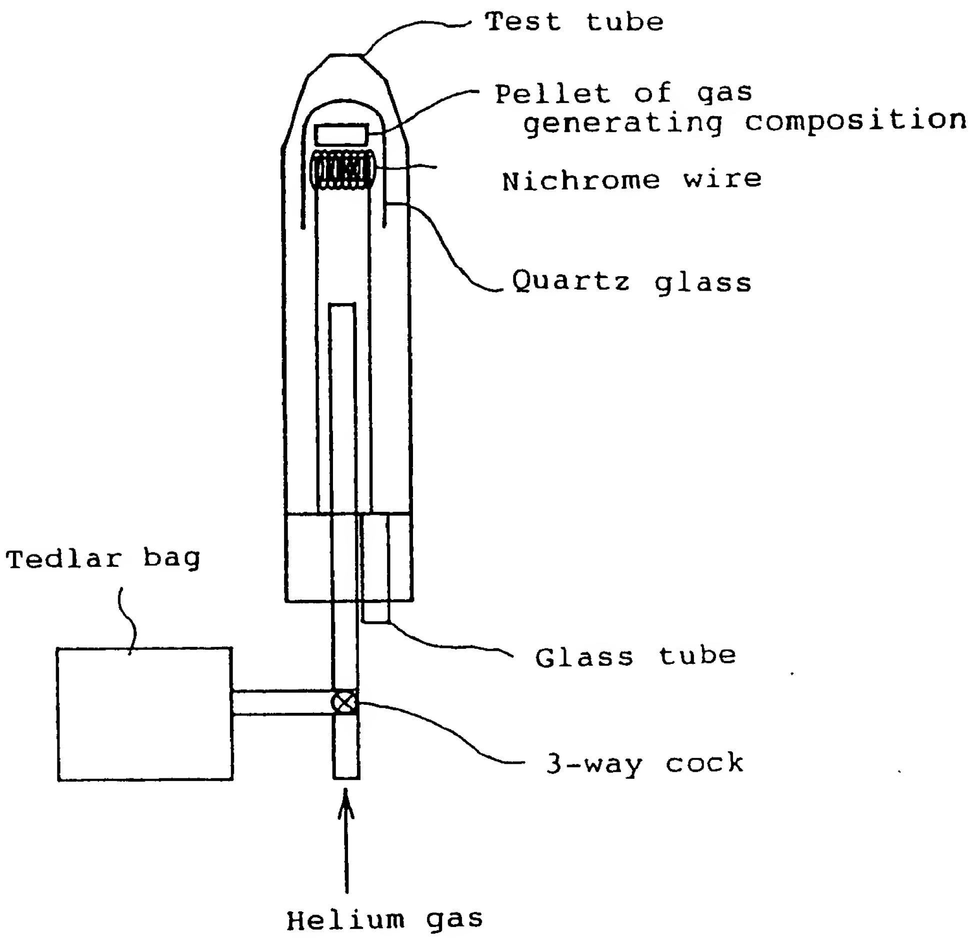
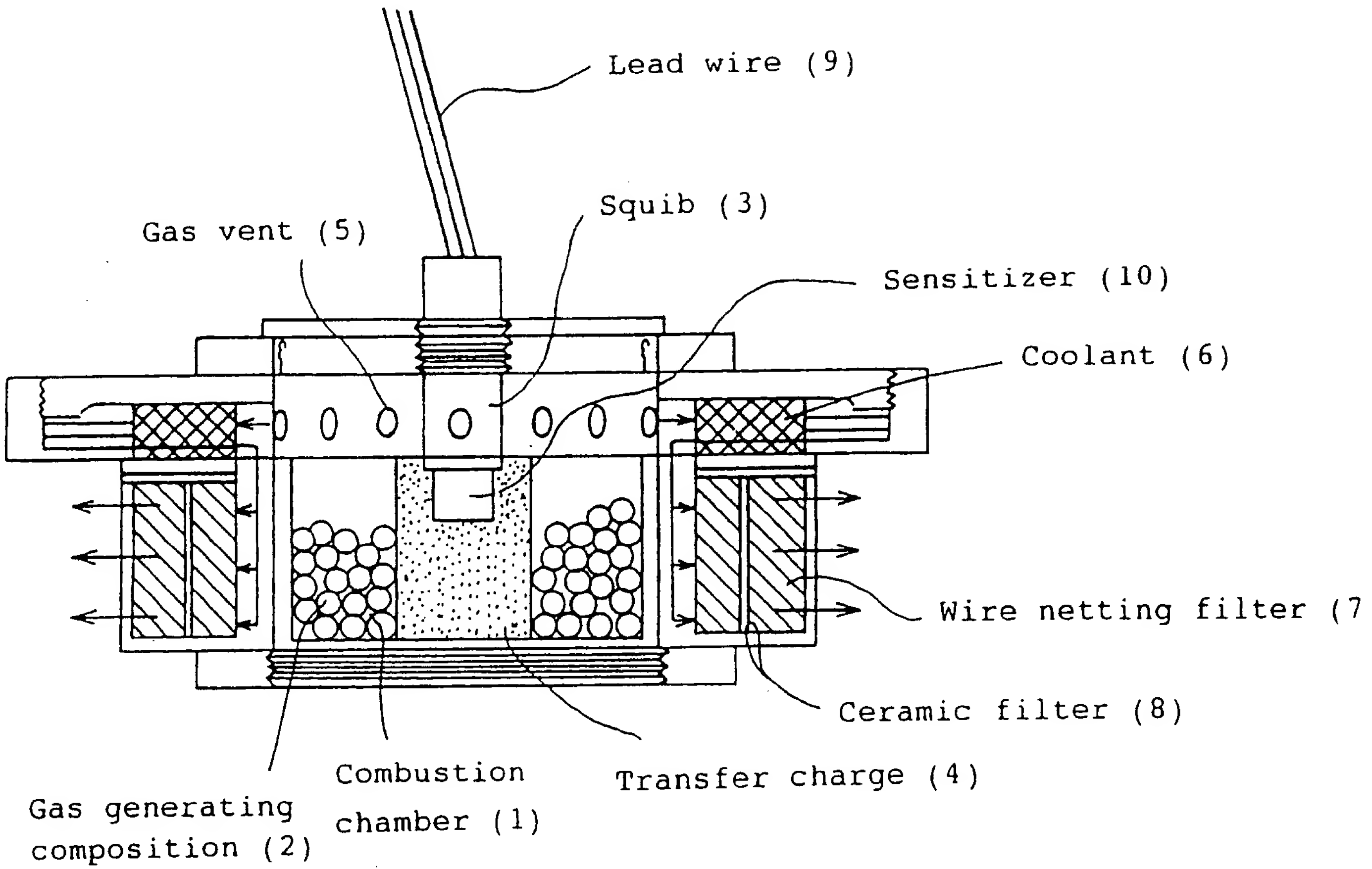

Test tube
Pellet of gas
generating composition
Nichrome wire
Quartz glass
Tedlar bag
Glass tube
3-way cock
Helium gas

FIG. 2



Lead wire (9)
Squib (3)
Gas vent (5)
Sensitizer (10)
Coolant (6)
Wire netting filter (7)
Ceramic filter (8)
Transfer charge (4)
Combustion chamber (1)
Gas generating composition (2)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/00199

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 C06D5/00, B60R21/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^6 C06D5/00, B60R21/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 6-239683, A (Daicel Chemical Industries, Ltd.), August 30, 1994 (30. 08. 94), Claim, lines 6 to 28, column 4, page 3 (Family: none)	1-2, 4-5 3, 6
Y	JP, 6-32690, A (Nippon Koki Co., Ltd. and two others), February 8, 1994 (08. 02. 94), Claim, lines 8 to 18, column 4, page 3 & WO, 94/01381, A1 & EP, 607446, A1 & CN, 1083463, A	1 - 6
Y	JP, 6-227884, A (Nippon Koki Co., Ltd. and two others), August 16, 1994 (16. 08. 94), Claim, line 43, column 3 to line 16, column 4, page 3, line 48, column 4, page 3 to line 24, column 5, page 4 & CN, 1083463, A	1 - 6
P,Y	JP, 8-12481, A (Otsuka Chemical Co., Ltd.),	6

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
May 28, 1996 (28. 05. 96)	June 4, 1996 (04. 06. 96)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/00199

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	January 16, 1995 (16. 01. 95), Claim, line 39, column 5, page 4 to line 35, column 7, page 5 (Family: none)	
X	JP, 51-25224, A (Allied Chemical Corp.), March 1, 1976 (01. 03. 76), Claim (Family: none)	7 - 10
X	JP, 47-27856, A (République Française), October 30, 1972 (30. 10. 72), Claim & CA, 941162, A1 & GB, 1371506, A & US, 3882673, A	7 - 10
X	JP, 50-112939, A (Eaton Corp.), September 4, 1975 (04. 09. 75), Claim (Family: none)	7 - 10
E,X E,Y	JP, 8-91167, A (Otsuka Chemical Corp.), April 9, 1996 (09. 04. 96), Claim, line 26, column 3, page 3 to line 18, column 5, page 4 (Family: none)	1-5, 7-10 6